

Topological effects in magnetic platinum nano-particles

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The magnetic properties of platinum nano-particles ranging in size from a few to up 300 atoms are investigated through first-principle calculations. It is found that the total magnetization depends strongly on the local atomic rearrangements, with an enhancement around five-fold axis. This is due to an elongation of the nearest neighbor distance together with a contraction of the 2nd distance, resulting in a net interatomic partial charge transfer from the atoms lying on the sub-surface layer (donor) towards the vertexes (acceptor).

The great scientific and technological interest in achieving better magnetic, optical, and catalytic devices has stimulated intensive research at the nanoscale, where small and finite size metallic nano-particles (mNP) offer the natural building blocks for a bottom up approach [1–5]. Indeed, for example in memory storage, a way to overcome the physical limits in down-scaling the dimensions of the magnetic components is to design and assemble mNP with controlled geometries in order to maximize the packing density and manipulate their mutual magnetic interaction, e.g., through doping with natural magnets as Fe and Co [6]. An intriguing possibility is the building of ‘super-atoms’, i.e., aggregates resembling the behavior of elemental atoms, even for magnetic purposes as shown by Vanadium and Cesium NP characterized by a magnetic moment as high as twice that of one Fe atom in its bulk [7, 8].

A long-standing puzzle of cluster physics is to understand how shape and composition influence the physico-chemical properties as a function of the mNP size: the problem is highly non-trivial because of the strong dependence of the electronic structure on the interatomic distances, which are highly distorted especially in non-crystallographic geometries [9, 10]. In transition metal nano-systems, partially occupied and energetically degenerate *d*-orbitals tend to retain to some extent their atomic character [8]. This can lead to high magnetic moments even in non-magnetic bulk species, such as Au, Pd, and Pt due to a non-uniform distribution of spins in the cluster [8, 11–27].

Pt is a transition metal that shows promising catalytic potential and for this reason its properties have been investigated at large. In recent superconducting quantum interference device experiments the magnetic properties of Pt NP synthesized by wet-chemistry techniques have been observed to depend strongly on the morphology where branched nano-systems are ferromagnetic whereas spherical symmetry induces paramagnetism with a blocking temperature higher than cubic motifs [25, 28]. Furthermore, surfactants are shown to enhance magnetic moments by breaking symmetry and inducing charge

transfer, raising the total magnetic moment in comparison with amine-coated Pt nano-materials, where the charge transfer is less efficient [17, 23]. Deliberately introducing certain geometrical deformations in Pt nano-wires should be considered as a further fundamental approach devoted to manipulate and tune the magnetic behavior in Pt nano-systems [29, 30]. Recent experiments show pronounced magnetic-conductance in atomic Pt contacts depending on their atomic configurations [31].

From a theoretical point of view, extensive numerical simulations based on density functional theory (DFT) have been performed to understand the magnetic nature of Pt thin films [32, 33] and nano-wires, where the appearance of ferromagnetism has been predicted only in certain structures [34, 35]. Nonetheless, only a few studies have been carried out on free Pt NP. In particular, Pt magnetism in nanoclusters has been associated with the partially filled *d* states [36]. The geometrical distortions characteristic of a finite nano-object can lead to a shift between minority and majority spin bands and thus less coordinated sites may show a higher magnetic moment [37]. However, what is the contribution of surface, vertex and core atoms and how an enhancement of the magnetism in Pt clusters is associated to geometrical factors have never been addressed from an atomistic point of view.

In this Letter, for the first time, the contribution to the total magnetization arising from different topological environments –surface-, vertex-, sub-surface- and core-atoms– in Pt NP has been calculated, via first-principle techniques. Different morphologies (icosahedra (Ih), decahedra (Dh), FCC and cubo-octahedra (CO)) for sizes up to 309 atoms have been considered. We find that an important role in understanding their magnetic properties is the charge transfer between the sub-surface vertex and the vertex. We believe part of this behavior to be generic, i.e., it could explain some of the magnetic properties of other nano-clusters like Au and Pd. Although a ferromagnetic ordering is always observed in any morphology, the total magnetic moment of icosahedral structures tops around 150 atoms and it is still considerable above zero

at 309 atoms, while dodecahedral motifs have a peak in their total magnetization below 100 atoms and then become gradually non-magnetic. The cubo-octahedra and truncated octahedra show a large constant magnetization of about $0.2 \mu_B/\text{atom}$ between 30 to 309 atoms, with a dip at 147 atoms. Quite surprisingly, we find that a high atomic polarization (AP) is not uniquely associated to atoms with a low coordination number. An interatomic Heisenberg charge exchange from sub-vertexes to the vertex determines, indeed, a large splitting of the majority and minority spin populations raising even more the AP. This charge transfer has been found to depend on the local topological environment and enhanced for vertex and sub-vertex lying on five-fold symmetry axes.

The magnetic behavior of Pt_N , where N is the total number of atoms in the cluster, is calculated using a plane-wave code based on density functional theory included in the Quantum ESPRESSO package [38]. Our analysis is not restricted to the *magic* sizes of Ih, Dh and CO shapes, corresponding to 13, 55, 147 and 309 atoms of the above polyhedra, but it includes: uncompleted and poly-icosahedral shapes at 38 and 76 atoms, since they have been found to be promising structural motifs for CoPt systems [39]; the Marks twinning of decahedra at 39 and 75 atoms, and a FCC motif at 76 atoms which corresponds to an incomplete octahedron at 85 atoms with a stacking fault and cuts to obtain (100) facets. All the configurations are ionically relaxed using the Broyden-Fletcher-Goldfarb-Shann's procedure available within the Quantum ESPRESSO package. Unrestricted local-spin polarized calculations are performed, where the exchange-correlation potential is described self-consistently within the generalized gradient approximation through the Perdew-Burke-Ernzerhof's functional [40], and the Rabe-Rappe-Kaxiras-Joannopoulos' ultrasoft pseudo-potential with non-linear core correction is used to model valence electron-nuclei interactions. The energy cut-off for the plane wave basis set is put at 45 Ry with a charge density cut-off of 360 Ry. Pt electronic configuration considered is $5d^9 6s^1$. Electronic eigenstates are calculated at the Γ point only. A Marzari-Vanderbilt's smearing [41] with 0.001 Ry as a degauss value is introduced [42]. Periodic boundary conditions are applied, and the simulation box includes at least 13 \AA of vacuum around the cluster to avoid any spurious effect between periodic images.

The macroscopic magnetism of the considered Pt morphologies is shown in Fig. 1, where the atomic averaged total magnetization (aTM), is plotted versus their size. For the sake of comparison, the dimer and the bulk values are added as reference points. The aTM is calculated as the total magnetization, M_{tot} , divided by the total number of atoms, N , i.e., $aTM = M_{tot}/N = \int n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r}) d\mathbf{r}/N$, where the integral runs over all space, while $n^\uparrow(\mathbf{r})$ and $n^\downarrow(\mathbf{r})$ are the electron charge densities for spin up and spin down, respectively. For CO

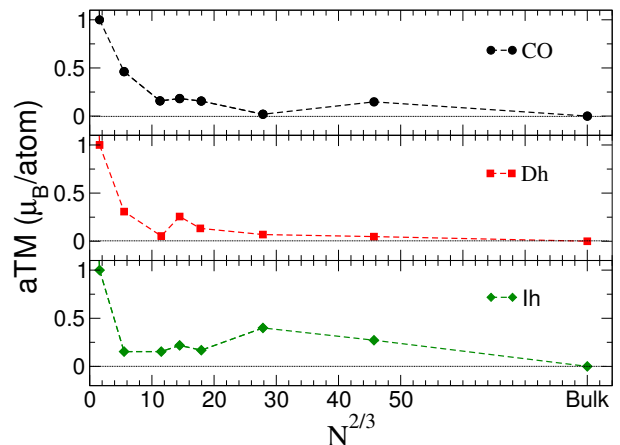


FIG. 1. (Color online) Atomic averaged magnetization, aTM , in μ_B/atom as a function of size $N^{2/3}$. The dimer and bulk values are included for comparison. Top panel CO and FCC-like structures; middle panel Dh; bottom Ih.

morphology, top panel of Fig. 1, the averaged total magnetic moment presents a flat region at $0.15\text{--}0.20 \mu_B/\text{atom}$ between 38 and 309 atoms, with an unexpected dip at 147 atoms. Decahedra peaks in their aTM at 55 atoms with $0.25 \mu_B/\text{atom}$ and then slowly decay to the asymptotic bulk paramagnetism. On the other hand, Ih patterns tops of the averaged total magnetic moment around 150 atoms after an almost constant behavior at smaller sizes. In the following we are going to argue that large aTM values are due to an inter-atomic contribution between sub-vertex atoms lying on the non-crystallographic five-fold axes and their vertex on top.

The origin of the magnetic properties in mNP can be rationalized in terms of two contributions: an intra-atomic and an inter-atomic charge transfer. The intra-atomic charge transfer induces an intra-band splitting between majority and minority population and gives rise to an atomic momentum around the Fermi energy. The inter-atomic charge transfer mainly occurs between atoms lying on consecutive shells, instead of intra-shell atoms, and therefore is strongly influenced by the local topology.

To investigate the relationship between the local environment and magnetic properties, atomic charges are computed performing a Bader analysis [43, 44] over the total as well as majority and minority spin charge densities. The Bader algorithm, indeed, searches the 2-D surface on which the charge density between atoms has a minimum and estimates the charge density inside the volume found for each atom. This methodology is a very efficient way to calculate the effective atomic charge. The charge transfer between shells is estimated in terms of atomic partial charge loss, CL^T , calculated as the difference between the total valence population owned by an atom and its nominal value of valence electrons me-

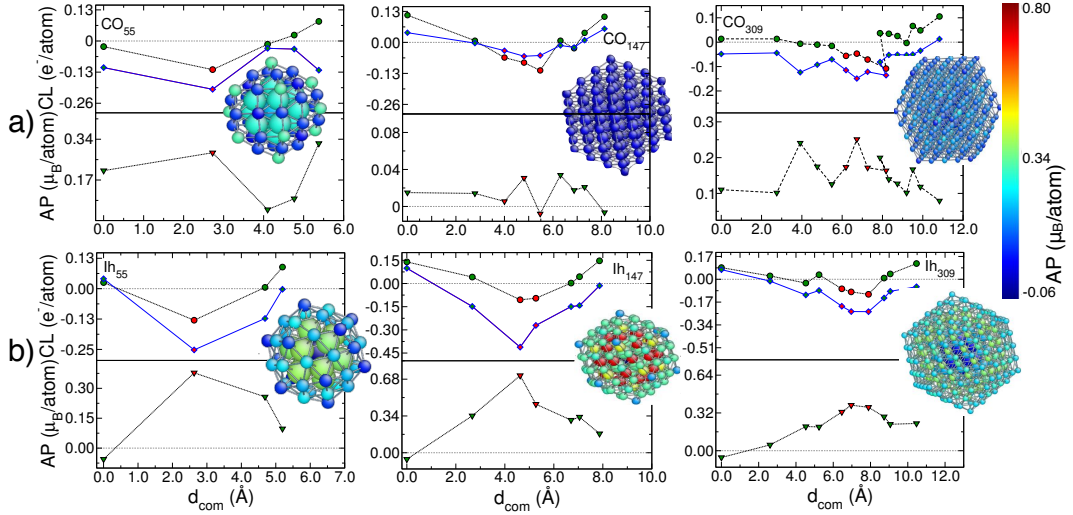


FIG. 2. (Color online) AP (triangle), total CL^T (circle) and minority CL^\downarrow (diamond) charge losses plotted against the radial distance, d_{com} for a) CO, and b) Ih shapes at various sizes up to 309 atoms. The symbol color indicates: red=sub-surface, green=other atoms. In the snapshots, atoms are colored according to their AP in temperature gradient as shown at the right: (blue) negative for partial charge donors and (red) positive for acceptors.

diated over the equivalent geometrical positions in each shell of a given morphology. For Pt, the nominal total valence population equals 10. The same approach is adopted to calculate the majority and minority splitting, the intra-atomic splitting, as a charge loss CL^\uparrow and CL^\downarrow , respectively, where the nominal value of valence electrons is now referred to as the up and down population in the bulk, 5 spins per Pt atom. The AP , or atomic magnetic moment, is then calculated as the difference between the majority and minority spin charge losses. The total and minority charge losses as well as AP are reported in Fig. 2 as a function of the radial distance from the centre of mass of the clusters d_{com} , for CO, and Ih, respectively. We want to point out how sub-vertices play an important role in the distribution of local magnetism. Since the smallest size, but where three shells could be drawn, those atoms are found to show a peculiar ability to act as donors (negative CL^T) of partial charge mainly towards the low coordinated vertexes (acceptors, positive CL^T). The charge donation is generally carried out by the minority population. On the other hand, surface atoms tend to act as acceptors allowing the majority band to accommodate the charge received. The inter-atomic charge transfer towards the innermost shells seems to be more complicated but is substantially still dominated by the sub-surface atomic behavior. Ih, independently of the size, shows a quite clear behavior both in the AP and CL s, see Fig. 2b. The sub-shell is highly polarized with a net charge transfer towards the vertexes of the cluster, leading to a significant magnetization in this morphology. The CO shape instead shows a more varied behavior, see Fig. 2a. For CO₅₅ and CO₃₀₉ there is a peak of AP in the sub-shell and some remnant

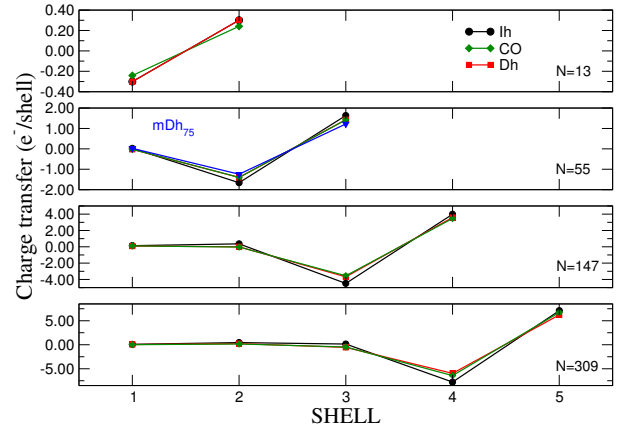


FIG. 3. (Color online) Total charge transfer (in electron per shell) between neighboring shells. A similar behavior is observed in all the nano-particles considered.

AP at the vertexes, also charge is transferred from the core and sub-shells to the surface. At both sizes there is a similar magnetization per atom. For CO₁₄₇, on the other hand, the AP is almost vanishing for each shell, and more significantly the magnetization essentially vanishes.

From Fig. 3, it is clear that a significant total charge transfer happens between the sub-surface and the uppermost layer. However, when local strain is present the distance between vertex and sub-vertex is shorter, allowing the outermost atoms to act as good charge acceptors. Five-fold sub-vertexes and vertexes present the shortest distance. The inter-atomic charge transfer contributes to the local magnetism by acting on the majority and minority population bringing a specific order to the

atomic polarization. On the other hand, there is another contribution to the magnetic properties that has to be taken into account, namely the intra-atomic band splitting, which is dominated by the minority charge loss. The intra-atomic band splitting is calculated from the total up/down charge loss and the analysis suggested in the following elucidates different mechanisms related to the local geometrical arrangements and the size of the NP. Crystalline-like shapes exhibit an initial intra-atomic charge exchange that decreases with the size of the cluster while Ih structures are found to show an extraordinary atomic magnetic moment at 147 atoms and a still pretty high TM value at 309 atoms. Dh NP (see Supplemental Material [45]), that contain crystallographic regions between five-fold axes, behave as a perfect mix up to 55 atoms while two well separated regions can be considered at bigger sizes: one along (100) direction characterized by non-magnetic atoms and the other along the 5-fold axis where the up/down splitting is still effective, therefore an analysis confined to the first coordination shell is not enough to explain this separation.

Mohn suggested that a further majority/minority band splitting can be justified by considering the effect of the 2nd nearest neighbor (NN) distance only if they are enough distorted with respect to their bulk value, where their contribution is considered negligible [46]. To understand the unexpected behavior of the CO_{147} magnetization we have investigated the distance distribution of first and second nearest neighbor of each vertex and sub-vertex. In Fig. 4 we report the vertex and sub-vertex 1st NN distances; the average distance between vertex and its 2nd NN lying on the (100) and on (111) surfaces, for CO_{147} , CO_{309} , Ih_{147} , and Ih_{309} . All distances are reported in lattice parameter. These geometries exhibit a contraction of the 1st NN distance with respect to their bulk value. However, we observe a stronger compression along the radial direction core-sub-vertex(SV)-vertex(V), than in the intra-shell directions, see Fig. 4 panes a) and c). This seems to justify a charge transfer from SV towards the core and V, thus generating a finite magnetic moment. Moreover, the 2nd NN distances between vertex and (111) surface atoms are always elongated, 4 b), leading to a reduction of the intra-shell charge transfer. This effect can further enhance the majority/minority band splitting. However, in CO, this effect is partially compensated because the V and (100) atoms 2nd NN distance is slightly contracted. A further look at the CO_{147} reveals that the intra-shell is similar to the inter-shell separation. This results in an additional charge transfer between the atom of either the surface or the 1st sub-shell, then reducing the effective magnetism as observed in Fig. 2.

To summarize, spin-polarized density functional simulations are carried out to calculate the total magnetization of crystallographic and non-crystallographic Pt nano-particles for sizes up to 309 atoms. It is observed

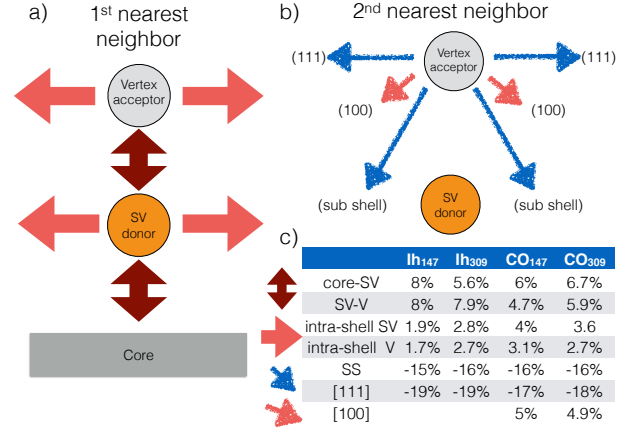


FIG. 4. (Color online) a) Schematic network of NN average distance of vertex (V) and sub-vertex (SV). Double arrows stand for inter-shell length while single arrow refers to intra shell distances. b) Schematic 2nd NN network around V: towards (111) surface atoms, common for both Ih and CO; atoms belonging to (100) facets, only for CO. c) Taking the DFT bulk lattice parameter as reference, the Table reports the relative value of the core-SV, SV-V, intra-shell SV, intra-shell V, V-sub shell (SS), (111) 2nd NN, and (100) 2nd NN distances. A positive (negative) value corresponds to a contraction (elongation) with respect to the bulk length.

that an enhanced magnetism appears in Dh (see Supporting Information) and especially in Ih Pt clusters, while in CO and FCC-like the average magnetization has a almost flat behavior from 36 to 309 atoms (with the notable exception of 147). Through a Bader estimate of the effective atomic charges, we have found that the atomic magnetic properties of Pt_N are ruled not only by the intra-atomic splitting of the up/down bands, but also by the inter-atomic charge transfer between sub-vertexes (donors) and vertexes (acceptors). This contribution is considerable for atoms lying on a five-fold axis. Our results demonstrate that the local topology plays a more fundamental role in explaining the high magnetic moment of Pt nano-particles than the coordination number itself. In fact, although our results show that a reduced coordination number can lead to a net atomic magnetization, especially in CO-like motifs, the sub-vertexes atoms along non-crystallographic axis in Ih and Dh are responsible of the enhancement of the atomic polarizability even though their coordination is twelve. This indicates that the electronic structure and thus the magnetic properties are influenced by the local environment, in particular associated with the contraction of the inter-shell distance between the two uppermost layers and the elongation of the second nearest neighbor distances between vertex and (111) surface atoms.

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